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A review on bio-oil production from biomass by using pyrolysis method

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ABSTRACT

The paper provides an updated review on thermal conversion of biomass for the production of liquid products referred as bio-oil. This technology is described focusing on the characterization of feedstock, reactor design, products formation and upgrading. For feedstock characterization is covered in terms of several pretreatment methods. The reactor designs are illustrated number of design ranging from fixed bed to circulating fluidized bed. The properties of bio-oil composition have caused increasingly extensive research to be undertaken to address properties that need modification and this area is reviewed in terms of physical, catalytic and chemical upgrading. The mechanism of the products formation is also illustrated by several chemical routes. Reactor parameters such as heating rate, temperature of pyrolysis, catalysts etc are reviewed.

Contents

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1. Introduction

The need for energy is increasing sharply due to the rapid increase in the world's population and developing technologies, while the current energy resources with limited reserves are decreasing. Biomass (plant materials) has been recognized as a major world renewable energy source to supplement declining fossil fuel resources. It is composed mainly of carbohydrate compounds (cellulose, hemicellulose, lignin and minor amounts of other organics) which are determined as the elements of carbon, hydrogen and oxygen and posses a high energy content [1,2]. Biomass energy is destined to play an important role in the future energy systems of the world.

Bio-oil known as pyrolysis oil, bio-fuel oil, pyrolytic oil and liquid wood [3,4] that was produced by pyrolysis of biomass. Generally, it can be found in a dark brown organic liquid form [4–6]. The bio-oil contains hundreds of organic compounds that belong to alkanes, aromatic hydrocarbons, phenol derivatives and little amounts of ketones, esters, ethers, sugars, amines and alcohols with H/C molar ratio higher than 1.5 [7,8]. It is produce by high thermal decomposition (pyrolysis) method without the additional of O_2/air.

The pyrolyze bio-oils can be directly used as fuels in boilers or subsequently upgraded to produce fuels and bulk chemicals using several methods such as zeolite cracking [9–11], hydrogenation [12–15] and aqueous phase processing [16,17]. Table 1 shows the type of biomass use in the production of bio-oil by various research work and the type of biomass obtain for this study.

This review mainly focuses on feedstock characterization, reactor type for fast and slow pyrolysis, product composition and upgrading. In the review for fast pyrolysis, our literature reviews more focus on data obtains beyond 2005 and above. Since more recent review article summarize from 2000 to 2005 [33].

2. Feedstock characterization

In order to achieve the high bio-oil yields of fast pyrolysis it is also necessary to prepare the solid biomass feedstock in such a manner that it can facilitate the required heat transfer rates. However, the type of feedstock also gives big role to achieve higher yield of bio-oil. Commonly, the land biomass residues were most familiar feedstock to produce pyrolysed oil are as rape and sunflowers [34], herbs residue [35], rice husk [36–38], cotton stalk [39], corn stalk [40], sugarcane bagasse and coconut shell [41]. However, the maximization of feedstock uses not limited to land biomass. The pyrolysis of microalgae also gave a good intention as can found in the literature [42–47].

Microalgae have so far received more than macroalgae for biofuels production [48], which can be cultured on a large-scale with supply of nutrients or waste water in coastal areas of East Asian countries including Korea. It can be cheap feedstock supplied for bio-oil production while it naturally grow absorbing phosphorus and nitrogen compounds which can minimizes the cost of production [49]. The various type of biomass contains different compositions of major component namely cellulose, hemicelluloses and lignin as shown in Table 2.

The elemental composition (C, H, O, N and S), ash content, moisture content and higher heating value (HHV) are determine to study the ability of biomass to produce high value of bio-oil. The elemental analysis and physical properties of biomass as a feedstock were summarized in Table 3.

2.1. Other metal contains in the feedstock

Refers to previous work on metals composition in feedstock, it was found that the Ca alkali metal shown the highest value in the

Table 2
General composition of various feedstocks for bio-oil production.

Composition	EFB [50]	Corn stover [51]	Poplar aspen [52]	Wheat straw [51]
Cellulose (mf wt%)	59.7	31.0	42.3	32.4
Hemicellulose (mf wt%)	22.1	43.0	31.0	41.8
Lignin (mf wt%)	18.1	13.0	16.2	16.7

Table 1
Type of biomass to produce bio-oil.

Biomass type	Type of reactor	Temp. (°C)	Bio-oil yield (wt%)	Type of pyrolysis	References
Grape bagasse	Stainless steel fixed-bed reactor	550	27.6	Fast pyrolysis	[18]
Hardwood & softwood from pine tree	Turbular vacuum pyrolysis reactor	450	55.0	Fast pyrolysis	[19]
Municipal, livestock and wood waste	Internal circulating fluidized-bed (ICFB) reactor	500	39.7	Fast pyrolysis	[20]
Plant thistle, *Onopordum acanthium* L.	Fixed-bed reactor	550	27.3	Slow pyrolysis	[21]
Potato skin	Stainless steel fixed-bed reactor	550	24.8	Steam pyrolysis	[22]
Pinewood sawdust	Conical spouted bed reactor	500	75.0	Flash pyrolysis	[23]
Pine wood	Auger reactor	450	50.0	Fast pyrolysis	[24]
Waste furniture sawdust	Fluidized-bed reactor	450	65.0	Fast pyrolysis	[25]
Rice husks	Fluidized-bed reactor	450	60.0	Fast pyrolysis	[26]
Sugar cane waste	Fixed-bed fire-tube heating reactor	475	56.0	Fast pyrolysis	[27]
Corn cobs & corn stover	Bubbling fluidized bed reactor	650	61.6	Fast pyrolysis	[28]
Laurel (*Laurus nobilis L.*) extraction	Fixed-bed reactor	500	21.9	Fast pyrolysis	[29]
Corncob	Fluidized-bed reactor	550	56.8	Fast pyrolysis	[30]
Jute stick	Continuous feeding fluidized bed reactor	500	66.7	Fast pyrolysis	[31]
Apricot pulp	Fixed-bed reactor	550	22.4	Fast pyrolysis	[5]
Wood sawdust	Cyclone reactor	650	74.0	Fast pyrolysis	[32]

Table 3
Elemental composition and physical properties of various biomass.

Biomass type	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)	Ash (wt%)	Moisture (wt%)	HHV (MJ/Kg)	References
Birch wood	49.05	6.28	44.17	0.16	–	0.30	–	18.40	[53]
Rice husks	48.36	5.13	32.79	0.72	0.31	12.50	6.80	16.79	[41]
Rapeseed	58.51	8.57	23.46	3.67	–	5.78	5.15	26.70[a]	[54]
Birch wood	48.45	5.58	45.46	0.20	–	0.30	5.26	17.02	[55]
Walnut shell	50.58	6.41	41.21	0.39	–	1.40	8.11	19.20[a]	[56]
Safflower	59.05	8.87	26.72	3.03	–	2.33	6.04	23.86[a]	[57]
Sesame stalk	48.62	5.65	37.89	0.57	–	7.26	9.53	19.10[a]	[58]
Soybean cake	52.46	6.17	26.51	8.72	–	6.15	9.15	23.23	[59]
Cardoon	42.78	4.40	43.69	0.64	0.09	8.40	–	18.20	[60]
Hybrid poplar wood	49.40	6.00	43.10	0.23	0.05	1.20	5.00	19.74	[61]
Mixed wood	47.58	5.87	42.10	0.20	0.03	2.10	7.76	–	[62]
Sweet gum wood	49.50	6.10	44.60	–	–	–	–	–	[63]
Peach pulp	44.51	6.73	45.38	0.88	–	2.40	9.30	15.40	[5]
Rice straw	36.89	5.00	37.89	0.40	–	19.80	–	16.78	[64]
Coconut shell	47.97	5.88	45.57	0.30	–	0.50	–	19.45	[65]
Pine wood	45.92	5.27	48.24	0.22	–	0.35	7.99	18.98[b]	[66]
Almond shell	47.63	5.71	44.48	–	–	2.18	–	–	[67]
Beech sawdust	48.60[b]	–	–	–	–	–	–	–	[68]
Olive husks	50.90	6.30	38.60	1.37	0.03	2.80	8.50	–	[69]
Timber wood	47.72	5.54	44.85	0.89	–	1.00	–	–	[70]

[a] Assumed higher heating value in a dry basis.
[b] Dry ash-free basis.

feedstock of 0.5 wt%, followed by K, Mg and Na of 0.7, 0.5 and 0.1 wt%, respectively [71–73]. From further study has been done by Mourant et al. [73], it was noted that the removal of alkaline species from the mallee wood prior to pyrolysis did not result in any significant change in the yields of bio-oil, bio-char or gas [74]. The reported data provide evidence that the effects of alkaline species removal on the bio-oil yield would be dependent on the type of biomass and/or that the bio-oil yields alone is not always identified as the best indicator to monitor the changes in the reaction pathways during pyrolysis.

2.2. Feedstock pretreatments

Cunha et al. [75] were reported that the treatment of biomass before convert to bio-oil will be produce high quality of products. The hydrolysis was carried out under acidic, basic or sequential acid/base treatments at 25 °C or 122 °C at ambient pressure for 1 h. In fact, by acid treatment method, the oxygen content was slightly reduced influence by oxygen-rich compound removal during treatment [76,77].

The presence of inorganic species in bio-oil also greatly influences the subsequent use of bio-oil. For example, the alkali and alkaline earthmetallic (AAEM) species are also associated with the accelerated ageing of bio-oil [78], thus contributing to modifications of the physical properties of bio-oil during storage. The pretreatment via water-washing can be removes of more than 70% of AAEM species from the biomass substrate. However, it will change of water content in the bio-oil product. In other hand, the removal of remaining 25% of AAEM species by acid washing resulted in almost 5% reduction in the water content of bio-oil. The formation of water during biomass pyrolysis remains a topic of debate [79–83].

2.3. Particle size of feedstock

Particle size of biomass feedstock has a major influence on the heating rate of solid fuel, making it an important parameter controlling the rates of drying and primary pyrolysis and to what extent these processes overlap during fuel decomposition. In fact, lower yields of liquids were measured when pyrolysing larger feedstock particles [84,85], as a result of the particle size effect on the secondary reactions of volatiles. For example, Nik-Azar et al. [85] found that an increase of particle size from 53–63 mm to 270–500 mm leads to a decrease of the maximum tar yield from 53% to 38% (mass % of parent fuel).

Table 4
Particle size distribution of EFB [50,90].

Feedstock particle size (μm)	Mass fraction	Average ash (mf wt%)
Less than 250	22	7.44
25–355	30	5.29
355–500	42	4.82
More than 500	6	4.72
Mass average	–	5.39

In fluidized bed experiments at 500 °C [86], the effect of particle size on the secondary conversion of tars was also suspected during pyrolysis of fine fuel particles (3–12 mm). The maximum bio-oil yield (58 wt% of biomass feed) was obtained at a reaction temperature of 500 °C with a particle size of 212–425 μm [87]. The smaller desired size of biomass particles is the more expense added to the feedstock preparation costs. To put this in perspective, a study conducted by Himmel et al. [88] showed that reducing biomass to particles in the size range of 2.5 mm to 250 μm would add $1.80/ton to $5.60/ton, respectively.

In the early days of fast pyrolysis development researchers thought that particle sizes of a few hundred microns were needed to facilitate the high heat transfer rates. However, more recent practical experience has demonstrated this is not the case, but sizes of approximately 2 mm are still necessary [89].The particle size was influence the mass fraction and average ash of the EFB particle size as shown in Table 4.

As it is well known, the feedstock with high value of ash and in particular potassium would led to reduce liquid yields in the fast pyrolysis [91]. In other works, the high ash content of original straw would be tends to promote chars forming reactions during pyrolysis [92–95]. Moreover, these are typical observations made from fast pyrolysis of agricultural residues [96] or energetic crops such as switch grass [94,97,1] which are all characterized by high ash contents.

3. Reactor types

From previous works, bio-oil has been produced by fluidized catalytic cracking method (FCC) [98], fluidized-bed [31], auger reactor [99,24], fixed-bed reactor [100,5], bubbling fluidized-bed reactor [28] etc.

3.1. Fast pyrolysis

Biomass fast pyrolysis is a novel and most effective method to convert biomass into liquid products with yields as high as 80% based on dry feed uses [101], which is a rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, char, and gas. The conditions required for fast pyrolysis process namely, dry feedstock needed (less than 10%), small particles (less than 3 mm), short residence times (0.5–2 s), moderate temperatures (400–500 °C), rapid quenching at the end of the process and gave the typical yields of bio-oil, char and gaseous products of 60–70%, 12–15% and 13–25%, respectively.

This process very good in process which can be operates at atmospheric pressure and modest temperatures (450 °C), while yielded high poduct of bio-oil exceed to 70 wt%. However, the fast pyrolysis will be produce high oxygen and water content of pyrolysis liquids makes them inferior to conventional hydrocarbon fuels. Moreover, the phase separation and polymerization of the liquids and corrosion of containers make storage of these liquids difficult. Fig. 1 shows a schematic diagram of the fluidized-bed reactor system for biomass fast pyrolysis. It was mainly consisted of gas-supplying unit, gas pre-heater, fluidized bed reactor, condenser, filters, accumulative flow meter and gas-collecting unit [102,30,98].

3.1.1. Bubbling fluidized bed

As we known, the bubling fluidized bed reactors have been used in petroleum and chemical processing for over fifty years and therefore have a long operating history. As reactor designs, they are characterized as providing high heat transfer rates in conjunction with uniform bed temperatures, both being necessary attributes for fast pyrolysis. By selecting the appropriate size for the bed fluidizing media, the gas flow rate can be established such that gas/vapor residence time in the freeboard section above the bed can be set to a desired value, generally between 0.5 and 2.0 s.

Generally, the operating temperature of 500–550 °C in the bed will usually result in the highest liquid yields at about 0.5 s residence time, however the larger systems can operate at a somewhat lower temperature and a longer residence time. The temperatures may also vary depending on the type of biomass being processed. In other hand, by direct heating using flue gases is not recommended because it can result in smaller oil yields due to oxidation from excess air in the flue gases. Heat supplied externally to bed, good mass & heat transfer and requires small biomass particles (2–3 mm).

In principle, the bubbling bed is "self cleaning" which means that char as a byproduct is carried out of the reactor with the product gases and vapors. However, in practice this requires using carefully sized feedstock with a relatively narrow particle size distribution. In cases of biomass particles are too large, the remaining char particles (after pyrolysis) may have too much mass to be effectively entrained out of the reactor with the carrier gas and product vapors. The density of this char will be less than that of the fluidizing media and, consequently, this char will "float" on top of the bed. In this location it will not experience enough turbulence with the bed media to undergo attrition into smaller particles that will eventually leave the reactor. A schematic of a typical fluidized bed is shown below in Fig. 2.

Another issue with having the char on top of the bed is that it will have a catalytic influence on the vapors as they pass through it on their way out of the bed. This can affect the yields and the chemical nature of the resulting liquid product. On the other hand, if fines are present in the feed, then the feed must be introduced lower in the bed otherwise the fines will be quickly entrained out of the bed before complete pyrolysis can occur. In general, char accumulation in the bed should be prevented. The design should include a means for skimming and discharging char from the top of the bed. If this is not done the feed will need to be carefully screened to obtain a narrow particle size distribution. This in turn will add considerably to the feedstock preparation costs.

There are some design considerations in bubling fluidized bed systems such as heat can be applied to the fluid bed in a number of different ways that offer flexibility for a given process. The vapor residence time is controlled by the carrier gas flow rate. For biomass feed particles, it was found that the particles size less

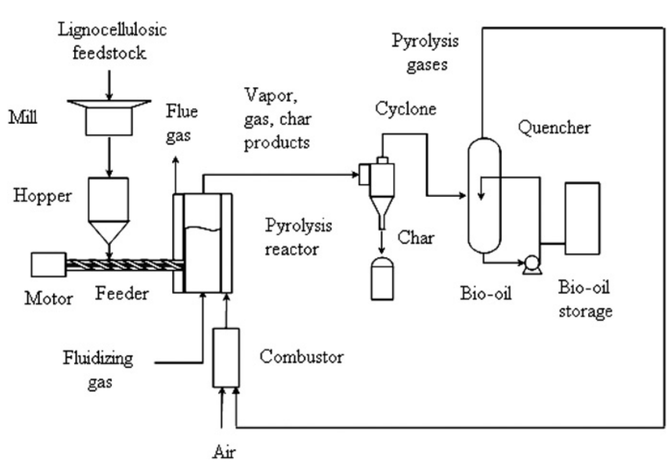


Fig. 1. Fast pyrolysis systems.

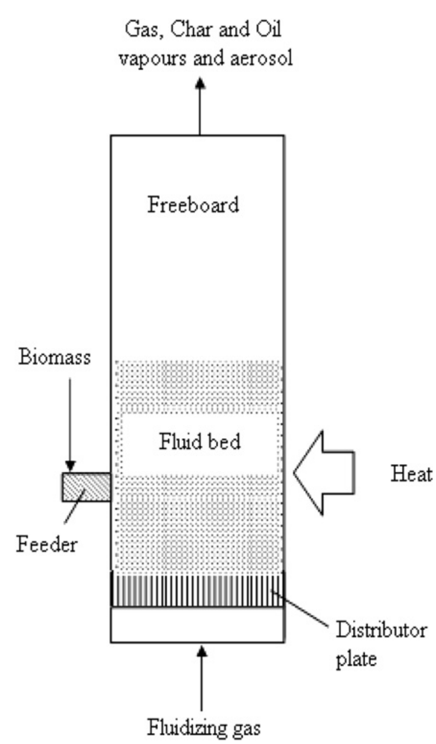


Fig. 2. Process schematic for bubbling fluidized bed.

than 2–3 mm are needed. The char produced in this process can catalyze vapor cracking reactions, so it needs to be removed from the bed quickly. In addition, the char also can accumulate on top of the bed if the biomass feed is not sized properly, so provisions for removing this char may be necessary. However, this process has problems in scale up purpose whereas heat transfer to bed at large scales has not been demonstrated.

3.1.2. Circulating fluidized bed

This reactor design also is characterized as having high heat transfer rates and short vapor residence times which makes it another good candidate for fast pyrolysis of biomass. It is somewhat more complicated by virtue of having to move large quantities of sand (or other fluidizing media) around and into different vessels. The hot sand was circulated between combustor and pyrolyzer units. This type of solids transport has also been practiced for many years in refinery catalytic cracking units, so it has been demonstrated in commercial applications. Circulating bed technology has been extensively applied to biomass pyrolysis by Ensyn Technologies under the name of Rapid Thermal Processing (RTP). Furthermore, various system designs have been developed with the most important difference being in the method of supplying heat. Earlier units were based on a single indirectly heated reactor, cyclone and standpipe configuration, where char was collected as a byproduct as well as heat supplied from the burning of char. A schematic of this type of pyrolysis system is shown below in Fig. 3.

Feed particles sized for a circulating bed system must be even smaller than those used in bubbling beds. In this type reactor the particle will only have 0.5–1.0 s (s) residence time in the high heat transfer pyrolysis zone before it is entrained over to the char combustion section in contrast to the bubbling bed where the average particle residence time is 2 s to 3 s. For relatively large particles this would not be enough time to transport heat to the interior of the particle. This is especially true as a char layer develops on the outside surface, which acts as an insulating layer preventing further penetration of heat. The movement of sand and particles through the system causes abrasion of this char layer but mostly at the elbows and bends where there is more forceful interaction between the particles and sand. The incompletely pyrolyzed larger particles will end up in the char combustor where they will simply be burned. Consequently, if larger feed particles are used, the oil yield will be reduced due to combustion of incompletely pyrolyzed particles. Particles in the 1–2 mm are the desired size range.

3.1.3. Rotating cone pyrolyzer

The Rotating Cone Pyrolysis Reactor has been under development at the University of Twente in The Netherlands since the early 1990s. Recent activities have involved scale up of the system to 200 kg/h. This technology is analogous to the transported bed design (circulated fluidized bed) in that it co-mingles hot sand with the biomass feed to affect the thermal pyrolysis reactions. The primary distinction is that centrifugal force resulting from a rotary cone is used for this transport instead of a carrier gas as described in Fig. 4. The biomass feed and sand are introduced at the base of the rotating cone while spinning causes centrifugal force to move the solids upward to the lip of the cone. As the solids spill over the lip of the cone, pyrolysis vapors are directed to a condenser. The char and sand are sent to a combustor where the sand gets re-heated before introducing at the base of the cone with the fresh biomass feed.

This design has demonstrated yields of 70% on a consistent basis. From this proposed design, it was identified two advantages namely, ease in products recovery and reducing wear problems. It was compact in design and does not require a carrier gas for pyrolysis (but it does for sand transport) which makes bio-oil product recovery easier. The transport dynamics of the sand and biomass are not as aggressive as in the Ensyn Rapid Thermal Processing (RTP) circulating fluid bed process therefore reducing wear problems. However, it was found that some weakness of this process design of integrated process and scale up issue. For this rotating cone pyrolyzer, the integrated process is complex, involving a rotating cone, a bubbling bed for char combustion, pneumatic transport of sand back to the reactor and hard in scale up purposes.

3.1.4. Vacuum pyrolysis

Pyrovac in Québec, Canada has developed a vacuum pyrolysis process for converting biomass to liquids. While this is a slow pyrolysis process (lower heat transfer rate) it generates a chemically similar liquid product because the shorter vapor residence time reduces secondary reactions [103]. However, the slow heating rates

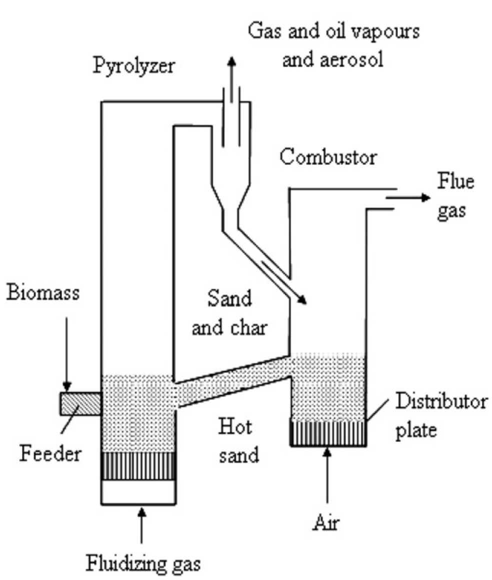


Fig. 3. Process schematic for Circulating fluidized bed.

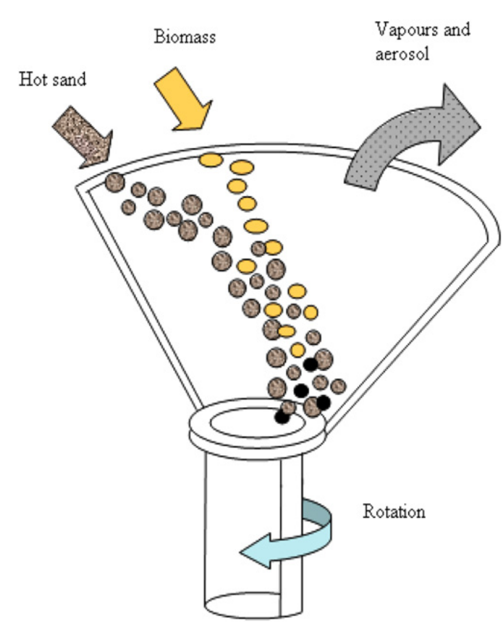


Fig. 4. Process schematic for rotating cone pyrolyzer.

also result in lower bio-oil yields of 30–45 wt% compared to the 70 wt% reported with the fluid bed technologies. For this vacuum pyrolysis, biomass was moved by gravity and rotating scrappers through multiple hearth pyrolyzer with temperature increasing from 200 °C to 400 °C. It can use larger particles and employs a little carrier gas during process. The process itself is very complicated mechanically, involving a moving metal belt that carries the biomass into the high temperature vacuum chamber. There are also mechanical agitators that periodically stir the biomass on the belt; all of this mechanical transport is being done at 500 °C. The schematic design of vacuum pyrolysis was described in Fig. 5.

These design features are expected to have high investment and maintenance costs. Operating at a vacuum requires special solids feeding and discharging devices to maintain a good seal at all times. Heating efficiency is low and, in this particular design, unnecessarily complex in the use of a burner and an induction heater with molten salts as a heat carrier. Even with these drawbacks vacuum pyrolysis does have several advantages in terms of products quality, liquid product condensation, particles size, ease in component extraction. From this pyrolysis process, it can be produces a clean oil (no or very little char) without using hot vapor filtration (this technique is discussed in section 2.5). Furthermore, the liquid product condensation is easier than for fluidized bed or entrained flow technologies (higher vapor concentration, less, if any, aerosol formation). As comparison, this reactor design can use larger feed particles than fluidized bed processes; up to 2–5 cm. The lignin-derived fraction of the oil can be of a lower molecular weight than that from fast pyrolysis processes, which may have advantages if extracting this component for phenolic type chemicals.

However, vacuum pyrolysis technology also has serious drawbacks for producing liquids, especially for fuel applications because of the high yields required a slow pyrolysis process that will not be able to provide oil yields as high as fast heating rate processes (vacuum pyrolysis has demonstrated yields of 47% organics and 17% water from spruce, 35% organics and 20% water from bark). Besides, it can be generates more water than other fast pyrolysis processes. In the Pyrovac plant the condensates are collected as two fractions, the second one being heterogeneous. Based on the published yields, after mixing these fractions the whole bark oil will contain 36% water and the wood oil 28% water, which can both result in phase separation which generates liquid effluents as volatile material that is not collected in the scrubbers but absorbed in the liquid ring compressor pump. These would need to be recycled back to the scrubbers. As a result, the scale up work for this reactor process is difficult as well as high cost of vacuum pump.

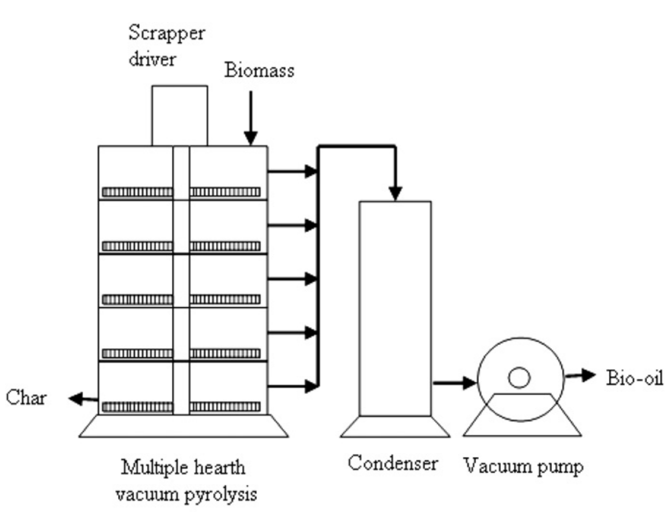


Fig. 5. Process schematic for vacuum pyrolysis.

3.1.5. Auger reactor

Previous works, the Auger type of pyrolyzer has been identified as especially appealing for its potential to reduce operating costs associated with bio-oil production. However, it was suitable for the small scale pyrolysis process [104]. Inside the reactor, the hot sand and biomass were mixed by Auger system. The process requires hot, heating and circulation system. The operating principle of this design is that biomass is continuously pyrolyzed by being brought into direct contact with a bulk solid heat transfer medium referred to as a "heat carrier." The heat carrier material, such as sand or steel shot, is heated independently before being metered into the reactor. On a gravimetric basis, thermodynamic calculations suggest a heat carrier feed rate 20 times the biomass feed rate. Two intermeshing, co-rotating augers quickly combine biomass and heat carrier in a shallow bed to effectively carry out the pyrolysis reactions. This mechanical mixing process, though not well understood, appears to be the essence of this alternative pyrolyzer design. Volatile vapors and aerosols exit at various ports, while char is transported axially through the 20" long reactor section and stored in a canister with the heat carrier. A detail of the stainless steel augers is depicted in Fig. 6.

3.2. Slow pyrolysis

Even the fast pyrolysis most popular and chosen technique for bio-oil production, the slow pyrolysis was also gives high attention in term of products obtained. Gercel [21] was reported that the slow pyrolysis with low heating rate of about 7 °C/min produced up to 24–43% of bio-oil. However, previous work shows that the slow pyrolysis would be obtained high level of char of 34–63 wt% at the pyrolysed temperatures of 500 °C [47,46].

From other study by Ucar and Karagoz [105], it obtained maximum oil yield of 21.98% at 500 °C at 30 °C/min heating rate with high carbon value. In another study, the slow pyrolysis of the straw and stalk of the rapeseed plant in a tubular reactor under the conditions of static atmosphere was carried out in the temperature range of 350–650 °C. The maximum bio-oil yield of about 18% was obtained at 650 °C at 30 °C/min heating rate [106].

The comparison study was done by Duman et al. [107], it was found that the slow pyrolysis of cherry seeds biomass produce medium level of bio-oil with 21 wt%, while the fast pyrolysis for

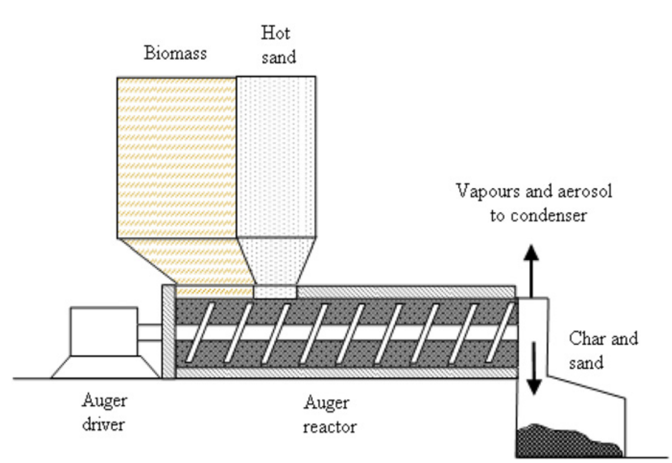


Fig. 6. Process schematic for auger reactor.

the same feedstock gave high bio-oil yield of about 44%. From that we can summarized that the slow pyrolysis is practically less efficient in terms of bio-oil yield and high level of char production compared to fast pyrolysis system.

4. Products formation

Biomass is a complex material, mainly composed of hemicellulose, cellulose and lignin in addition to extractives (tannins, fatty acids, resins) and inorganic salts. Cellulose is the most important element in biomass due to its large proportion. Cellulose forms the framework of the biomass cell walls which are composed of the cohesive, interlaced cellulosic microfibrils matrix deposited by hemicellulose, lignin, proteins and pectins [108,109]. The cellulose has crystalline and amorphous zones according to the microfibrils periodically or randomly distributed along the orientation of cellulose fibrils. The amorphous zone is more actively than the crystalline zone, adding the complexities in thermal decomposition of cellulose [110]. It is found that the primary structure of cellulose is a linear homopolymer of glucopyranose residues linked by b-1, 4-glycosidic bonds, while the glucopyranose comes from the hemiacetal reaction of D-glucose between C-1 and C-5 positions (Fig. 70 [111,112]. The degree of polymerization of the native celluloses (n) depends on the source and is considered to be from 6000 to 8000 for those fromwoods [110].

The understanding of pyrolytic behavior of cellulose is fundamental to biomass thermochemical conversions. Early work for cellulose pyrolysis outlines the classic kinetic schemes of three main chemical pathways [113,114]. It is found that: low-temperature delays the initial process, corresponding to a reduction in the degree of polymerization and the formation of the so-called 'anhydrocellulose' or 'active cellulose'; high temperature pyrolysis of cellulose is expressed by two competitive degradation reactions, the first essentially to char and gas, the second to tars (mainly levoglucosan as shown in Fig. 7). The notion of 'anhydrocellulose' is excluded in the recent work [115] which explains cellulose decomposition solely by two competitive reaction channels, one ascribed to the formation of tars (mainly levoglucosan) and char, the other to the light gases.

The formation of 'anhydrocellulose' has been confirmed [115], but the formation of light gases is considered not directly to be related to the low-temperature step or 'anhydrocellulose'. Other kinetic schemes have been proposed, mainly the first-order reaction [116–118], to give better representation of the experimental cellulose pyrolysis. However those kinetic models have largely simplified the complexity of primary and secondary reactions during cellulose pyrolysis. Literature mostly concentrates on the mass loss, kinetic scheme and heat of the reaction. The chemical reactions, particularly the secondary reactions and the formation pathways of the typical products, have not been vigorously discussed. Recently combined analytical techniques, such as GC–MS and FTIR–MS, are employed to determine the product yield quantitatively [119–121]. Such techniques can be employed to improve the kinetics of cellulose pyrolysis with modified chemical pathways for the main products.

4.1. Chemical mechanism for biomass to bio-oil formation

During the pyrolysis process, it was obtained variable chemical components as called bio-oil. In this paper, the mechanism of major products, namely hydroxyacetaldehyde (HAA), levoglucosan (LG), furfural (FF) and aldehyde compounds will be discussed in Sections 4.1.1 to 4.1.3. The general mass percentage (%) of bio-oil composition based on pine and spruce feedstock was summarized in Table 5.

4.1.1. The mechanism of anhydro-sugars and the secondary cracking

Table 5 shows that levoglucosan (1,6-anhydro-*b*-D-glucopyranose) is the main component in the bio-oil (30%), confirming the results [115] that the initial thermal decomposition of cellulose is the depolymerization of the cellulose polymer to form various anhydrosugar derivatives, among which levoglucosan is the most prevalent. The yield of levoglucosan is affected by the source of the cellulose and the experimental conditions [122]. Table 5 shows that levoglucosan is reduced at higher temperature, in contrast other products (such as HAA, HA and 5-HMF), which implies a competitive mechanism between the levoglucosan and

Table 5
Bio-oil composition for mixture of pine and spruce feedstock.

Concentrations wt%	**Feedstock:** Pine 53% Spruce 47% (including bark) [127]	**Feedstock:** Palm Tree Empty fruit bunches (EFB) [127]
Methanol Insoluable Solids & Lignin	34.47	8.4
Cellobiosan (Cel)	2.21	3.2
Glyoxal	2.21	4.0
Hydroxyacetaldehyde (HAA)	14.12	15.4
Levoglucosan (LG)	8.72	30.4
Formaldehyde (FA)	4.15	2.4
Formic acid (FA)	5.12	9.1
Acetic acid (AA)	5.81	10.1
Acetol	6.64	1.7
1,6-anhydro glucoranose	Not report	3.1
Furfuryl alcohol (FF)	Not report	5.2
Catechol	Not report	5.0

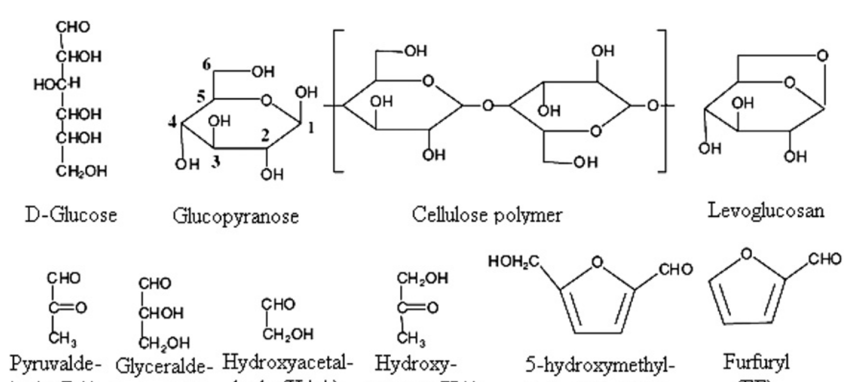


Fig. 7. The chemical structures of D-glucose, glucopyranose, cellulose polymer and the typical chemical components of bio-oil.

other products. Similar results have been reported [123,119] claiming that the fragments from the ring opening reactions are enhanced under the high temperature by competing for active cellulose monomer with the levoglucosan (Fig. 8). Such phenomenon is also observed for the long residence time at reduced feeding flow rate, which can be interpreted as the sequential mechanism between the levoglucosan and other products, according to the research [115,119,121,123,125]. Therefore it could be claimed that levoglucosan also acts as an intermediate for the formation of the other products in the cellulose pyrolysis such as hydroxyacetone, 5-hydroxymethyl-furfural and hydroxyacetaldehyde.

The formation of levoglucosan from cellulose pyrolysis has been proposed as the cleavage of the 1,4-glycosidic linkage in the cellulose polymer followed by intramolecular rearrangement of the monomer units [126]. A similar pathway (2) in Fig. 8 is developed to express the formation of levoglucosan (LG). The 1,4-glucosidic bond is presumably cleaved by the acetal reaction between C-1 and C-6, evolving the hydroxyl radical from C-6, then the free hydroxyl radical coalesces with the disrupted glucosidic bond on C-4 to form levoglucosan (1,6-anhydro-*b*-D-glucopyranose). It is thought that the evolution of the hydroxyl group (free radical) from the C-6 position might be the initiator for the formation of levoglucosan.

Other anhydrous hexoses, such as anhydro-D-mannose and 1,6-anhydro-glucofuranose, are the isomers of levoglucosan, whose formation is similarly initiated from the free hydroxyl radicals and followed by the chemical structure rearrangement (pathway (1) in Fig. 8). However the reactions of such rearrangement require more energy while competing with the secondary cracking [115,119,123], therefore these anhydrous sugars only occupy a small portion of the bio-oil comparing to levoglucosan (Table 5). Noticeably, the yield of 2,3-anhydro-D-mannose are enhanced by the elevated temperature at the expense of anhydro-D-mannose. Both of them are increased with the longer residence time, since the formation reactions are predominant over their secondary cracking reactions. The yields of the 1,6-anhydroglucofuranose is improved at higher temperature when more energy is available for the rearrangement reactions, on the other hand, longer residence time reduces its yield overwhelmed by the secondary reactions.

The secondary decomposition of anhydrous sugars (especially levoglucosan) is shown in Fig. 9, while the pathways are developed based on the progress in [115,119,120,121,126]. It demonstrates that thermal decomposition of levoglucosan proceeds through the ring-opening of the glucosidic 1,6-acetal bond and the rehydration to form glucopyranose monomer, followed by the prompt secondary reactions. Three main sets of chemical pathways are proposed to describe the possible fission of the glucopyranose: pathway (8) suggests a ring-opening by breaking the ring glucosidic bond and the bond between C-2 and C-3 to form HAA (hydroxyacetaldehyde) and a tetrose (four-carbon atoms) fragment; pathway (9) breaks the ring to formaldehyde and a pentose fragment; pathway (10) forms a hexose chain by the fission of hemiacetal bond on C-1 position. The possible routes of the secondary decomposition of the (C4–6) fragments in Fig. 9 explain the formation of the various products under the high temperatures, through the possible dehydration, hydration, fission, decarbonylation and decarboxylation reactions.

4.1.2. Mechanism of 5-hydroxymethyl-furfural (5-HMF) and furfural (FF) production

The formation pathways for 5-HMF and FF have not been studied thoroughly in the literature, two the chemical pathways are developed in this work: one is the direct ring-opening and rearrangement reactions of cellulose unit molecules (pathway (5) in Fig. 8); the other is the secondary reactions of levoglucosan (pathway (10) to (16) in Fig. 9). The pathway (5) is initiated by the cleavage of the ring glucosidic bond on cellulose unit to form an aldehyde-structure on C-1, followed by the formation of double bond on C-4 and C-5 through the chain structure rearrangement. Another double-bond on C-2 and C-3 is formed through the dehydration of the corresponding hydroxyl groups. Then, the acetal reaction of the hydroxyl groups on C-2 and C-5 is taken as the essential step to form 5-HMF.

The secondary reactions of levoglucosan to produce 5-HMF (pathway (10) to (16) in Fig. 9) has been proposed before [126], where the pyran-ring is initially cleaved to the hexose chain structure, followed by dehydration of the hydroxyl groups and sequential acetal reaction on C-2 and C-5. Regardless the origin of

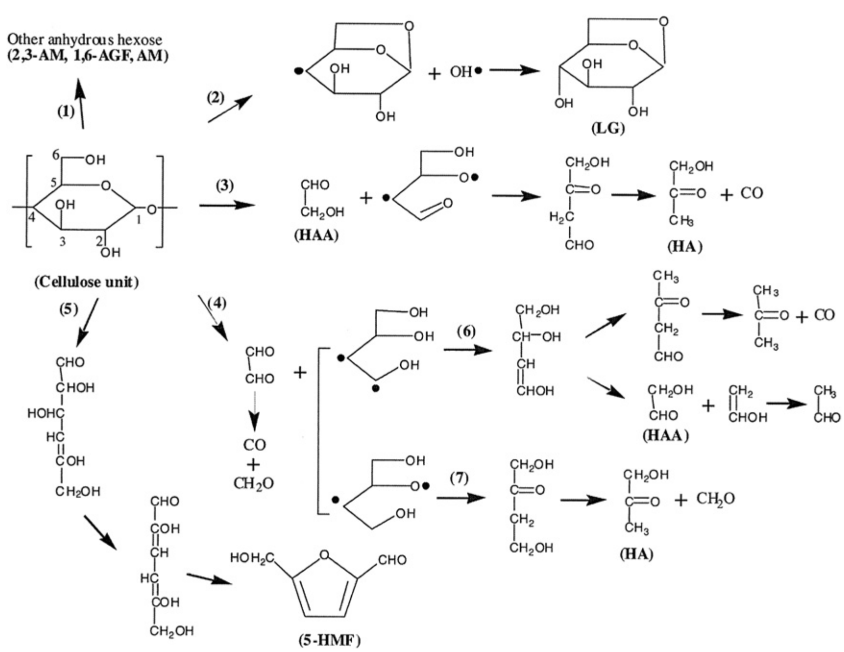


Fig. 8. The chemical pathways for the direct conversion of the cellulose molecule [124].

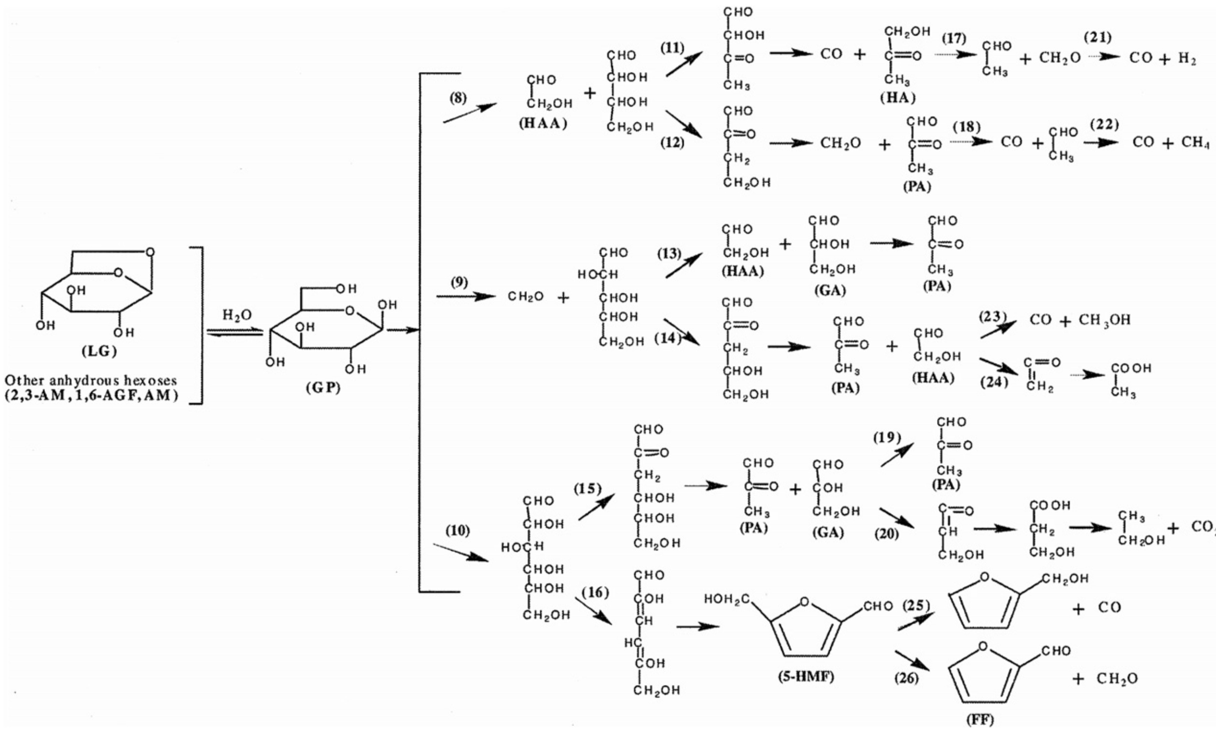


Fig. 9. The chemical pathways for the secondary decomposition of the anhydrosygars (especially levoglucosan) [124].

the 5-HFM, the furfural (FF) is approved to be produced from the secondary reaction of 5-HFM (pathway (26) in Fig. 9), along with the formation of formaldehyde through the dehydroxymethylation reaction of the side chain of the furan-ring. Another pathway has been proposed for the secondary reaction of 5-HMF [126], suggesting the rearrangement reaction to form aryl compounds, such as benzene and phenol, which are detectable in the bio-oil but not presented in Table 5.

4.1.3. Mechanism of hydroxyacetaldehyde production

Hydroxyacetaldehyde (HAA) is a major component of a group of the C2–4 oxygenated products in the bio-oil from the cellulose pyrolysis, along with hydroxyacetone (HA), glyceraldehyde (GA) and pyruvaldehyde (PA) [115,119,125,128]. The formation of the products from decomposition of sugar or cellulose was discussed based on the chemical pathways in Figs. 8 and 9. The well-established chemical pathway for the formation of HAA is presented as the pathway (3) in Fig. 8 and (8) in Fig. 9. The ring hemiacetal bond is very active under the thermal conditions and the bond between C-2 and C-3 is longer than other positions of the ring [115], hence, the HAA is easily produced on the C-1 and C-2 by the ring-opening through the cleavage of the above two active bonds, along with a four-carbon fragment. It is also suggested that almost all of the carbons on the ring could contribute to the formation of HAA [119].

The pathways (4) to (6) in Fig. 8 forms the HAA on the C-5 and C-6 through the cleavage of the rearranged four-carbon fragment. Another pathway (9) to (13) in Fig. 9 presents the formation of HAA on the C-2 and C-3 from the scission of the five-carbon fragment, while HAA is formed on the C-5 and C-6 through the pathway (9) to (14) in Fig. 9. It is concluded that the HAA is preferably formed from the C-1 and C-2, and C-5 and C-6. The decomposition of HAA under the high temperature is proposed to comply with the two chemical pathways (23) and (24) in Fig. 9. One (pathway (23)) is to produce CO and methanol through the decarbonylation reaction, while the other one (pathway (24)) undergoes the dehydration to be ketene structure and the sequential rehydration to the acetic acid.

The pathways (3) and (4) to (7) in Fig. 8 present the possible routes to produce HA (hydroxyacetone) through the cleavage of the four-carbon fragments from the direct conversion of the cellulose molecules. The HA produced from the decomposition of levoglucosan is speculated to proceed in only one pathway (8) to (11), where the tetrose fragment is initially dehydrated on C-5 and C-6 and then cleaved to CO and HA by the decarbonylation on C-3 [115]. It is assumed that the HA is mainly produced from the direct conversion of cellulose molecules and partly from the secondary decomposition of levoglucosan, since higher temperature improves the HA yield more substantially than longer residence time. The decomposition of HA is proposed to undergo the pathway (17) in Fig. 9 to produce acetaldehyde and formaldehyde, which are the precursors for the formation of CO and methane [126].

In addition, the GA (glyceraldehyde) is an important intermediate for the formation of PA (pyruvaldehyde) through the dehydration reaction, such as the pathway (9) to (13) and (10) to (15) to (19) in Fig. 9. Other pathways for the formation of PA are proposed as (8) to (12) and (9) to (14), indicating that PA could be produced from the secondary reactions of the C3–6 fragments in Fig. 9. Comparatively, the PA is hardly produced from the direct fission of cellulose molecules while there is no reasonable pathway for the formation of PA in Fig. 8. This indicates that the PA is mainly from the secondary decomposition of levoglucosan, explaining that the yield of PA improves more with longer residence time than under higher temperature. The decomposition of PA is believed to produce CO and acetaldehyde by the decarbonylation reaction [119].

The GA (C3 fragment) undergoes the pathway (10) to (15) to (20) to produce propionic acid, followed by the decarboxylation reaction for CO_2 along with the formation of alcohol as shown in Fig. 9. The acidic compounds in bio-oil from cellulose pyrolysis are produced by the dehydration of the aldehyde alcohol structure to a ketene structure, and then rehydration to the acidic

products (such as the pathway (9) to (14) to (24)), according to [115,119,125,128]. It is believed that the C2–6 fragments with the structure of aldehyde–alcohol could potentially produce the acidic compounds through the dehydration, rearrangement and rehydration reactions.

4.2. Pyrolysis reaction parameters

Many pyrolysis parameters such as feed particle size, temperature, heating rate, residence time, different atmospheres, biomass type and catalyst, strongly affect the yield and properties of the products have been extensively studied in the past 20 years [129–134].

4.2.1. The influence of heating rate and pyrolysis temperature

The most important and significant parameter in bio-oil production process is effect of heating rate and reaction temperature on products yield. It is known from the literature survey and previous studies that pyrolysis temperature plays an important role on product distribution [21,135–138]. The faster heating rates at a temperature of about 500 °C maximize the yield of bio-oil [139,91], while low heating rates favor the formation of char [86,13,40]. Williams and Nigrinad [140] was reported that the pyrolysis of rice husks was carried out in fuidized bed reactor shown an increased in the production of carbon monoxide in gas products with increase pyrolysis temperature.

In the other work, Abnisa et al. [141] was reported that the pyrolysis temperature (biomass type- palm tree empty fruit bunch) of 400 °C to 500 °C shown the bio-oil yield increased from 36.8 wt% to 46.1 wt%. The bio-oil yields were sharply increased about 9.3 wt% with a ratio 100 °C. However, the bio-oil yields were decreased from 42.9 wt% to 35.6 wt% at temperature of 600 to 800 °C. It can be explained that bio-oil yields decreased by the decreases of the organic and specific products and secondary cracking of volatiles at temperature above 500 °C [142]. The cracking has led to more resulting in higher volume of gaseous products which were also observed at other biomass wastes in the literatures [143,144].

4.2.2. The influence of catalyst presence

In addition, the effect of catalyst presence in pyrolysis reaction also well studied by researchers. Ates & Aslı Isıkdag [145] was reported that the oil yields of 22.2% obtained without catalyst were increased to 24.1% by using alumina catalyst. While, the gas yields of 29.9% and 30.9% obtained without catalyst was decreased to 28.5% and 24.1% using a catalyst at low and moderate temperatures, respectively.

Pyrolysis of olive and hazelnut bagasse biomass samples with two selected catalysts, namely activated alumina and sodium feldspar, have been conducted in a fixed-bed reactor [146–148]. The maximum bio-oil yields for the bio-oils obtained from pyrolysis of olive bagasse were found as 37.07% and 36.67% on using activated alumina and sodium feldspar as catalysts, respectively, while these values were 27.64% and 31.68%, respectively, for the bio-oils from hazelnut bagasse. Both catalysts have significant effects in the view of decreasing the bio-oil yield when it is compared to non-catalytic case. These results are consistent with those obtained from some of the previous studies [140,149].

4.2.3. Effect of feedstock types

The various feedstocks included palm oil-based, sunflower, cassava stalk, rhizome and rice husk shown the different yield of bio-oil as summarized in Table 6. The feedstock types can plays a big role to produce higher yield of bio-oil because of the different composition in the biomass as shown in Table 2 previously. The higher content of cellulose in feedstock was observed that give higher amount of bio-oil parallel to the products mechanism as shown in Section 4.1.1.

Table 6
Bio-oil yield based on various feedstock types.

Type of feedstock	Yield of bio-oil (wt%)	References
Palm oil (palm shell)	47.3	[141]
Sunflower-oil cake	48.69	[150]
Cassava stalk	62	[151]
Cassava rhizome	65	[151]
Rice husk	41.7	[152]

Table 7
Physical properties of bio-oil.

Material	pH	Density (kg/m^3)	Viscosity at 40 °C (cSt)	Ash content at 575 °C (wt%)	Water content (wt%)	References
Soybean oil cake	3.82	0.993	62	0.30	0.001	[164]
Switch grass	3.29	1.13	60.9	0.40	24.7	[165]
Linseed	4.00	1.08	58	0.50	21.5	[153]

4.3. Bio-oil characterization

The detailed bio-oil characteristics have been extensively studied by researchers for land biomass from 2005 to 2011 [153–161].

The water content is an important issue on bio-oil production process. High amounts of water present in bio-oil are one of the major drawbacks for its utilization as a fuel. Cornelissen et al. [162] were reported that the flash co-pyrolysis of biomass (willow) with polylactic acid (PLA) can be obtained high yield of bio-oil with lower water content of 28%. It was clearly that PLA shows to have a positive influence on the energetic value of the bio-oil produced and on the resulting energy recuperation. In addition, Acikgoz & Kockar [153] were reported that the slow pyrolysis oil of linseed (*Linum usitatissimum* L.) contained 21.5% of water.

Commonly, the maximum water content has been identified is 25–26 wt% [163], while the literature reports a water content between 15% and 30% and even more [3,97]. The physical properties of bio-oils based on ASTM standard test method were summarized in Table 7.

The bio-oil produce from pyrolysis consist of many contaminant which were caused the low valuable of the products. The liquid product may also be upgraded to refined fuels, added to petroleum refinery feed stocks or may contain chemicals in economical recoverable concentrations. The bulk densities and calorific values of the liquid and solid products are high which were resulting in a high energy density compared to the original biomass [106,166,167]. There were many research focused on treatment to increase the quality of bio-oil. The oxygen content of bio-oil is the major problem which is limited it as fuel source [9,10,168,169].

5. Upgrading

5.1. Hydrotreatment to reduce oxygen content

The first studies on the hydrotreatment of pyrolitic oils with the objective to reduce the oxygen content were performed by

Elliot et al. [170]. The reaction was performed in a bench scale reactor configuration consisting of two fixed bed reactors operated at 21 MPa hydrogen. The Ni–Mo and Co-Mo on alumina were used as the hydrotreating catalysts. The deoxygenation rate was found to be dependent on the liquid hourly spaced velocity (LHSV) and complete deoxygenation could be achieved at a LHSV of ca. 0.1 h^{-1}. Zheng & Wei [171] has been studied on the oxygen contents of the distilled bio-oil. It was shown that the distilled bio-oil has lower oxygen content of 9.2 wt% compared to fast pyrolysis bio-oil as well as higher heating value, lower corrosivity and better stability.

5.2. Supercritical water method to increase heating value

In other works, Duan & Savage [172] was upgraded the crude algal bio-oil using supercritical water method (SCW). The SCW treatment led to product oil with a higher heating value (~42 MJ/kg) and lower acid number than the crude bio-oil. The product oil was also lower in O and N and essentially free of sulfur. In the other hand, the upgrading of biomass pyrolytic oils by catalytic method is most interesting works that was zirconia/titania and a ZSM-5 formulation with the highest surface area could be yielded organic liquid products with reduced oxygen and higher aromatics content compared to the non-catalytic runs [173]. It will be led to increase bio-oil products by in-situ reaction at 500 °C.

5.3. Esterification bio-oils under atmospheric condition

Esterification of bio-oil with low molecular weight alcohols has been demonstrated as an effective approach to mitigate the deleterious properties of bio-oil. In the past few years, a great of endeavor has been devoted to upgrade bio-oils by esterification [174–176]. Zhang [177] and Xiong et al. [178] attempted to esterify bio-oils under atmosphere pressure using solid acid, solid base and acidic ion exchange resins as the catalysts. Their result showed that the acidity, density, heating value and storage stability of the bio-oil after treatment could be improved remarkably. Very recently, supercritical fluids were also employed in upgrading bio-oils. Peng et al. [179,180] surveyed the esterification of a bio-oil in supercritical ethanol. Tang et al. [181] combined hydrotreatment, esterification and cracking to upgrade bio-oil in supercritical ethanol under hydrogen atmosphere, and showed that the upgrading process performed effectively and the properties of the upgraded bio-oil were improved significantly.

5.4. Catalytic cracking of bio-oil into chemicals

In terms to increase value of bio-oils obtained from cheap biomass, it was high potential works to convert it into valuable chemicals such as the series of hydrocarbon-based products. Hydrocarbons are usually formed in very low yields during fast pyrolysis of biomass, but can be greatly increased by using proper cracking catalysts with deoxygenation capability [181]. Zeolite catalysts (such as HZSM-5, HY, etc.) are very effective to convert the highly oxygenated crude bio-oils or pyrolysis vapors to hydrocarbons which are dominated by several light aromatic hydrocarbons (benzene, toluene, xylene and naphthalene) [182,183]. For example, in the studies performed by Adjaye et al. [9,10], catalytic cracking of the crude bio-oil by HZSM-5 catalysts obtained a organic liquid product with up to 90 wt% of aromatic hydrocarbons, and the aromatic hydrocarbons contained abundant toluene (31.8 wt%) and xylene (33.1 wt%). In other work, Yu et al. [184] was reported the upgrading of bio-oil through one-step hydrogenation-esterification of furfural and acetic acid to produce alcohol and ester products. It was found that the efficient method for bio-oil upgrading that gave high selectivity to desired products (alcohol and ester) of 66.4% with the conversion of furfural is 56.9%.

Table 8
Upgrading for various uses and chemicals.

Composition in bio-oil	Uses	References
Levoglucosan	Food additive, pharmaceutical	[185,187]
Ethanol	Biofuel	[190]
Furfural	Pharmaceutical, pesticide	[191]
Acetic acid	Specialty chemical	[187]
Formic acid	Preservative, antibacterial agent	[149,187]
Hydroxyacetaldehyde	Fragrance substances, pharmaceutical intermediates	[14]

The treated bio-oil can be fractionating into many components such as levoglucosan [185], acetic acid, formaldehyde, formic acid, acetol, furfural and hydroxyacetaldehyde [186]. Levoglucosan is one of the major components in bio-oil and considered as a potential building block with large area of usage for synthesis of polymers, food additive, pharmaceuticals, pesticides, and surfactants [187,188]. The levoglucosan as one of the pyrolysis product can easily extract from the bio-oil by phase separation technique [189]. Microorganisms have been identified that can ferment levoglucosan to citric acid and itaconic acid. The various uses of bio-oil fractionation components were summarize in Table 8.

6. Conclusion

Bio-oil is recognized as a future commodity to substitute petroleum based fuel. However, the extent of research and large scale production is still very limited. The researchers mainly focus production of bio-oil in laboratory scale and also they did not focused mainly on characterization fuel parameters. These parameters should be compared to petroleum based fuel. The reactor designs are not given in detail to use for scale up studies. Feedstock characterization and pretreatment method are not considered for detail studies by many workers. Similarly upgrading although composition of the bio-oil discussed by many workers change a same this parameters on the composition are not recognize well since the avenue open for bio-oil production future researchers will focused on this issues.

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References

[1] Tsai WT, Lee MK, Chang YM. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reaction. Journal of Analytical and Applied Pyrolysis 2006;76:230–7.
[2] Kim SS, Kim J, Park YH, Park YK. Pyrolysis kinetics and decomposition characteristic of pine trees. Bioresource Technology 2010;1001:9797–802.
[3] Bridgwater AV. Biomass fast pyrolysis. Thermal Sciences 2004;8:21–49.
[4] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels 2004;18:590–8.
[5] Ozbay N, Apaydin-Varol E, Uzun BB, Putun AE. Characterization of bio-oil obtained from fruit pulp pyrolysis. Energy 2008;33:1233–40.
[6] Islam MR, Tushar MSHK, Haniu H. Production of liquids fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes. Journal of Analytical and Applied Pyrolysis 2008;82:96–109.

[7] Wu L, Guo S, Wang C, Yang Z. Production of alkanes (C7–C29) from different part of poplar tree via direct deoxy-liquefaction. Bioresource Technology 2009;100:2069–76.
[8] Qiang L, Wen-Zhi L, Xi-Feng Z. Overview of fuel properties of biomass fast pyrolysis oils. Energy Conversion and Management 2009;50:1376–83.
[9] Adjaye JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: conversion over various catalysts. Fuel Processing Technology 1995;45:185–202.
[10] Adjaye JD, Bakhshi NN. Production of hydrocarbon by catalytic upgrading of a fast pyrolysis bio-oil. 2. Comparative catalyst performance and reaction pathways. Fuel Processing Technology 1995;45:185–202.
[11] Hew KL, Tamidi AM, Yusup S, Lee KT, Ahmad MM. Catalytic cracking of bio-oil to organic liquid product (OLP). Bioresource Technology 2010;101:8855–8.
[12] Rocha JD, Luengo CA, Snape CE. The scope for generating bio-oils with relatively low oxygen contents via hydrpyrolysis. Organic Geochemistry 1999;30:1527–34.
[13] Zhang SP, Yan YJ, Li TC, Ren ZW. Upgrading of liquid fuel from the pyrolysis of biomass. Bioresource Technology 2005;96:545–50.
[14] Elliott DC. Historical developments in hydroprocessing bio-oils. Energy & Fuels 2007;21:1792–815.
[15] Elliott DC, Hart TR. Catalytic hydroprocessing of chemical models for bio-oil. Energy & Fuels 2009;23:631–7.
[16] Luque R, Clark JH, Yoshida K, Gai PL. Efficient aqueous hydrogenation of biomass platform molecules using supported metal nanoparticles on Starbons (R). Chemical Communications 2009:5305–7.
[17] Vispute TP, Huber GW. Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils. Green Chemistry 2009;11:1433–45.
[18] Demiral I, Ayan EA. Pyrolysis of grape bagasse. Effect of pyrolysis conditions on the product yields and characterization of the liquid product. Bioresource Technology 2011;102:3946–51.
[19] Ortega JV, Renehan AM, Liberatore MW, Herring AM. Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks. Journal of Analytical and Applied Pyrolysis 2011;91:190–8.
[20] Cao J, Xiao X, Zhang S, Zhao X, Sato K, Ogawa Y, et al. Preparation and characterization of bio-oils from internally circulating fluidized-bed pyrolyses of municipal, livestock, and wood waste. Bioresource Technology 2011;102:2009–15.
[21] Gercel HF. Bio-oil production from *Onopordum acanthium L.* by slow pyrolysis. Journal of Analytical and Applied Pyrolysis 2011;92:233–8.
[22] Onal EP, Uzun BB, Putun AE. Steam pyrolysis of an industrial waste for bio-oil production. Fuel Processing Technology 2011;92:879–85.
[23] Amutio M, Lopez G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. Resources, Conservation and Recycling 2012;59:23–31.
[24] Thangalazhy-Gopakumar S, Adhikari S, Ravidran H, Gupta RB, Fasina O, Tu M, et al. Physical properties of bio-oil produced at various temperature from pine wood using an auger reactor. Bioresource Technology 2010;101: 8389–95.
[25] Heo HS, Park HJ, Park YK, Ryu C, Suh DJ, Suh YW, et al. Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. Bioresource Technology 2010;101:S91–6.
[26] Heo HS, Park HJ, Park SH, Kim S, Suh DJ, Suh YM, et al. Fast pyrolysis of rice husks under different reaction conditions. Industrial & Engineering Chemistry 2010;16:27–31.
[27] Islam MR, Parveen M, Haniu H. Properties of sugarcane waste-derived bio-oils obtained by fixed-bed fire-tube heating pyrolysis. Bioresource Technology 2010;101:4162–8.
[28] Mullen CA, Boateng AA, Goldberg NM, Lima IM, Laird DA, Hicks KB. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. Biomass and Bioenergy 2010;34:67–74.
[29] Ertas M, Alma MH. Pyrolysis of laurel (*Laurus nobilis L.*) extraction residues in a fixed-bed reactor: characterization of bio-oil and bio-char, Journal of Analytical and Applied Pyrolysis. 88, 22–29.
[30] Zhang H, Xiao R, Huang H, Xiao G. Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor. Bioresource Technology 2009;100:1428–34.
[31] Asadullah M, Rahman MA, Ali MM, Motin MA, Sultan MB, Alam MR, et al. Jute stick pyrolysis for bio-oil production in fluidized bed reactor. Bioresource Technology 2008;99:44–50.
[32] Lede J, Broust F, Ndiaye F-T, Ferrer M. Properties of bio-oils produced by biomass fast pyrolysis in a cyclone reactor. Fuel 2007;86:1800–10.
[33] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 2012;38:68–94.
[34] Sanchez ME, Lindao E, Margaleff D, Martinez O, Mora A. Pyrolysis of agricultural residues from rape and suflowers: production and characterization of bio-oils and biochar soil management. Journal of Analytical and Applied Pyrolysis 2009;85:142–4.
[35] Wang P, Zhan S, Yu H, Xue X, Hong N. The effects of temperature and catalyst on the pyrolysis of industrial wastes (herb residue). Bioresource Technology 2010;101:3236–41.
[36] Lu A, Yang XL, Zhu ZF. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. Journal of Analytical and Applied Pyrolysis 2008;82:191–8.
[37] Guo X, Wang S, Wang Q, Guo Z, Luo Z. Properties of bio-oil from fast pyrolysis of rice husk. Chinese Journal of Chemical Engineering 2011;19:116–21.
[38] Zheng JL. Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system. Journal of Analytical and Applied Pyrolysis 2007;80:30–5.
[39] Zheng JL, Yi WM, Wang NN. Bio-oil production from cotton stalk. Energy Conversion and Management 2008;49:1724–30.
[40] Uzun BB, Sarioglu N. Rapid and catalytic pyrolysis of corn stalks. Fuel Processing Technology 2009;90:705–16.
[41] Tsai WT, Lee MK, Chang YM. Fast pyrolysis of rice husks: product yields and compositions. Bioresource Technology 2007;98:22–8.
[42] Miao X, Wu Q, Yang C. Fast pyrolysis of microalgae to produce renewable fuels. Journal of Analytical and Applied Pyrolysis 2004;71:855–63.
[43] Pan P, Hu CW, Yang WY, Li YS, Dong LL, Zhu LF, et al. The direct pyrolysis and catalytic pyrolysis of Nannochloropsis sp residue for renewable bio-oils,. Bioresource Technology 2010;101:4593–9.
[44] Peng W, Wu Q, Tu P, Zhao N. Pyrolytic characteristics of microalgae as renewable energy source determined by thermogravimetric analysis. Bioresource Technology 2001;80:1–7.
[45] Wu Q, Dai J, Shiraiwa Y, Sheng G, Fu J. A renewable energy source-hydrocarbon gases resulting from pyrolysis of the marine nanoplanktonic alga emiliania huxleyi. Journal of Applied Phycology 1999;11:137–42.
[46] Grierson S, Strezov V, Ellem G, McGregor R, Herbertson J. Thermal characterization of microalgae under slow pyrolysis conditions. Journal of Analytical and Applied Pyrolysis 2009;85:118–23.
[47] Grierson S, Strezov V, Shah P. Properties of oil and char derived from slow pyrolysis of Tetraselmis chui. Bioresource Technology 2011;102: 8232–8240.
[48] Bae YJ, Ryu C, Jeon JK, Park J, Suh DJ, Suh YW, et al. The characteristics of bio-oil produced from the pyrolysis of three marine microalgae. Bioresource Technology 2011;102:3512–20.
[49] Ryu JK, Cho JH, Kim DY. Strategies to industrialize the algae bio-business and policy direction (Korean), Policy Research 2009–2013. Seoul, Korea: Korean Maritime Institute; 2009.
[50] Abdullah N, Gerhauser H. Bio-oil derived from empty fruit bunches. Fuel 2008;87:2606–13.
[51] Scott DS, Piskorz J, Radlein D. Liquid products from the fast pyrolysis of wood and cellulose. Industrial & Engineering Chemistry Process Design and Development 1985;24:581–8.
[52] Scott DS, Piskorz J. The flash pyrolysis of aspen-poplar wood. Canadian Journal of Chemical Engineering 1982;60:666–74.
[53] Thunman H, Niklasson F, Johnsson F, Leckner B. Composition of volatile gases and thermochemical properties of wood for modeling of fixed or fluidized beds. Energy & Fuels 2001;15:1488–97.
[54] Onay O, Beis SH, Kockar OM. Fast pyrolysis of rape seed in a well-swept fixed bed reactor. Journal of Analytical and Applied Pyrolysis 2001;59:995–1007.
[55] Zanzi R, Sjöström K, Björnbom E. Rapid pyrolysis of agricultural residues at high temperature. Biomass and Bioenergy 2002;23:357–66.
[56] Onay O, Beis SH, Koçkar OM. Pyrolysis of walnut shell in a well-swept fixedbed reactor. Energy Sources 2004;26:771–82.
[57] Beis SH, Onay O, Koçkar OM. Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. Renew Energy 2002;26:21–32.
[58] Ates F, Putun E, Putun AE. Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil. Journal of Analytical and Applied Pyrolysis 2004;71:779–90.
[59] Uzun BB, Pütün AE. Fast pyrolysis of soybean cake: product yields and compositions. Bioresource Technology 2006;97:569–76.
[60] Encinar JM, González JF, González J. Fixed-bed pyrolysis of *Cynara cardunculus L.* Product yields and compositions. Fuel Processing Technology 2000;68:209–22.
[61] Agblevor FA, Besler S, Wiselogel AE. Fast pyrolysis of stored biomass feedstocks. Energy & Fuels 1995;9:635–40.
[62] Dupont C, Commandré JM, Gauthier P, Boissonnet G, Salvador S, Schweich D. Biomass pyrolysis experiments in an analytical entrained flow reactor between 1073K and 1273K. Fuel 2008;87:1155–64.
[63] Nunn T, Howard JB, Longwell JP, Peters WA. Product compositions and kinetics in the rapid pyrolysis of sweet gum hardwood. Industrial & Engineering Chemistry Process Design and Development 1985;24: 836–844.
[64] Raveendran K, Ganesh A, Khilar KC. Pyrolysis characteristics of biomass and biomass components. Fuel 1996;75:987–98.
[65] Fagbemi L, Khezami L, Capart R. Pyrolysis products from different biomasses:application to the thermal cracking of tar. Applied Energy 2001;69: 293–306.
[66] Sensöz S, Can M. Pyrolysis of pine (Pinus Brutia Ten.) Chips: 1. Effect of pyrolysis temperature and heating rate on the product yields. Energy Sources 2002;24:347–55.
[67] Balci S, Dogu T, Yücel H. Pyrolysis kinetics of lignocellulosic materials. Industrial & Engineering Chemistry Research 1993;32:2573–9.
[68] Barooah JN, Long VD. Rates of thermal decomposition of some carbonaceous materials in a fluidized bed. Fuel 1976;55:116–20.
[69] Di Blasi C, Signorelli G, Di Russo C, Rea G. Product distribution from pyrolysis of wood and agricultural residues. Industrial & Engineering Chemistry Research 1999;38:2216–24.
[70] Della Roca PA, Cerrella EG, Bonelli PR, Cukierman AL. Pyrolysis of hardwoods residues: on kinetics and chars characterization. Biomass and Bioenergy 1999;16:79–88.

[71] Li C-Z, Sathe C, Kershaw JR, Pang Y. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. Fuel 2000;79:427–38.
[72] Di Blasi C, Galgano A, Branca C. Influences of the chemical state of alkaline compounds and the nature of alkali metal on wood pyrolysis. Industrial & Engineering Chemistry Research 2009;48:3359–69.
[73] Mourant D, Wang Z, He M, Wang XS, Garcia-Perez M, Ling K, et al. Mallee wood fast pyrolysis: effects of alkali and alkaline earth metallic speciesBon the yield and composition of bio-oil. Fuel 2011;90:2915–22.
[74] Fahmi R, Bridgwater A, Donnison N, Yates N, Jones JM. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. Fuel 2008;87:1230–40.
[75] Cunha JA, Pereira MM, Valente LMM, de la Piscina PR, Homs N, Santos MRL. Waste biomass to liquids: low temperature conversion of sugarcane bagasse to bio-oil. The effect of combined hydrolysis treatments. Biomass and Bioenergy 2011;35:2106–16.
[76] Das P, Ganesh A, Wangikar P. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. Biomass and Bioenergy 2004;27:445.
[77] Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Industrial & Engineering Chemistry Research 2009;48:3713.
[78] Hoekstra E, Hogendoorn KJA, Wang XQ, Westerhof RJM, Kersten SRA, van Swaaij WPM. Fast pyrolysis of biomass in a fluidized bed reactor: in situ filtering of the vapors. Industrial & Engineering Chemistry Research 2009;48:4744–56.
[79] Kersten SRA, Wang XQ, Prins W, van Swaaij WPM. Biomass pyrolysis in a fluidized bed reactor. Part 1: literature review and model simulations. Industrial & Engineering Chemistry Research 2005;44(9):8773–85.
[80] Scheirs J, Camino G, Tumiatti W. Overview of water evolution during the thermal degradation of cellulose. European Polymer Journal 2001;37:933–42.
[81] Mamleev V, Bourbigot S, Le Bras M, Yvon J. The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis interdependence of the steps. Journal of Analytical and Applied Pyrolysis 2009;84:1–17.
[82] Chaiwat W, Hasegawa I, Kori J, Mae K. Examination of degree of cross-linking for cellulose precursors pretreated with acid/hot water at low temperature. Industrial & Engineering Chemistry Research 2008;47:5948–56.
[83] Chaiwat W, Hasegawa I, Tani T, Sunagawa K, Mae K. Analysis of cross-linking behavior during pyrolysis of cellulose for elucidating reaction pathway. Energy & Fuels 2009;23:5765–72.
[84] Scott DS, Piskorz J. The continuous flash pyrolysis of biomass. Canadian Journal of Chemical Engineering 1984;62:404–12.
[85] Nik-Azar M, Hajaligol MR, Sohrabi M, Dabir B. Effects of heating rate and particle size on the products yields from rapid pyrolysis of beech-wood. Fuel science & technology international 1996;14:479–502.
[86] Wang X, Kersten SRA, Prins W, van Swaaij WPM. Biomass pyrolysis in fluidized bed reactor. Part 2: Experimental validation of model results. Industrial & Engineering Chemistry Research 2005;44:8786–95.
[87] Islam MN, Zailani R, Ani FN. Pyrolytic oil from fluidised bed pyrolysis of oil palm shell and its characterization. Renew Energy 1999;17:73–84.
[88] Himmel M, Tucker M, Baker J, Rivard C, Oh K, Grohman K. Comminution of biomass: hammer and knife mills, Biotechnology and Bioenergy Symposium, No.15. John Wiley & Sons Inc. 1986.
[89] Bridgewater AV, Czernik S, Piskorz J, editors. Progress in thermochemical biomass conversion. Oxford: Blackwell Science; 2001.
[90] Abdullah N. An assessment of pyrolysis for processing empty fruit buches. PhD thesis. Aston University, Birmingham, UK, 2005.
[91] Chiaramonti D, Oasmaa A, Solantausta Y. Power generation using fast pyrolysis liquids from biomass. Renewable & Sustainable Energy Reviews 2007;11:1056–86.
[92] Auber M. Effet catalytique de certains inorganiques sur la sélectivité des réactions de biomasses et de leurs constituants, PhD thesis INPL-LRGP, Nancy, France, 2009.
[93] Agblevor FA, Besler S, Evans RJ. Inorganic compounds in biomass feedstocks: their role in char formation and effect on the quality of fast pyrolysis oils, Proceedings of biomass pyrolysis oil properties and combustion meeting, September 26–28, NREL-CP-430-7215 (1994) 77–89.
[94] Agblevor FA, Besler S. Inorganic compounds in biomass feedstocks. 1. Effect on the quality of fast pyrolysis oils. Energy & Fuels 1996;10:293–8.
[95] Jendoubi N, Broust F, Commandre JM, Mauviel G, Sardin M, Lédé J. Inorganics distribution in bio oils and char produced by biomass fast pyrolysis: the key role of aerosols. Journal of Analytical and Applied Pyrolysis 2011;92:59–67.
[96] Oasmaa A, Solantausta Y, Arpiainen V, Kuoppala E, Sipilä K. Fast pyrolysis bio-oils from wood and agricultural residues. Energy & Fuels 2010;24: 1380–8.
[97] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Organic Geochemistry 1999;30:1479–93.
[98] Zhang HY, Xiao R, Wang DH, Zhong ZP, Song M, Pan QW, et al. Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized catalytic cracking (FCC) catalysts. Energy & Fuels 2009;23: 6199–6206.
[99] Ingram L, Mohan D, Bricka M, Steele P, Strobel D, Crocker D, et al. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy & Fuels 2008;22:614–25.
[100] Eigenberger G. Fixed-bed reactors, Ullmann's Encyc1opedla of Industnal Chemistry. VCH Publisher Inc; 1992 vol B4.
[101] Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. Renewable & Sustainable Energy Reviews 2000;4:1–73.
[102] Zhang H, Xiao R, Wang D, He G, Shao S, Zhang J, et al. Biomass fast pyrolysis in a fluidized bed reactor under N2, CO2, CO, CH4 and H2 atmospheres. Bioresource Technology 2011;102:4258–64.
[103] Garcia-Perez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Vacuum pyrolysis of softwood and hardwood biomass comparison between product yields and bio-oil properties, Journal of Analytical and Applied Pyrolysis 78, 104–116.
[104] Bhattacharya P, Steele PH, El Barbary MH, Mitchell B, Ingram L, Pittman Jr CU. Wood/plastic copyrolysis in an auger reactor: chemical and physical analysis of the products. Fuel 2009;88:1251–60.
[105] Ucar S, Karagoz S. The slow pyrolysis of pomegranate seeds: the effect of temperature on the product yields and bio-oil properties. Journal of Analytical and Applied Pyrolysis 2009;84:151–6.
[106] Karaosmanoglu F, Tetik E, Gollu E. Biofuel production using slow pyrolysis of the straw and stalk of the rapeseed plant. Fuel Processing Technology 1999;59:1–12.
[107] Duman G, Okutucu C, Ucar S, Stahl R, Yanik J. The slow and fast pyrolysis of cherry seed. Bioresource Technology 2011;102:1869–78.
[108] Keegstra K, Talmadge KW, Bauer WD, Albersheim P. The structure of plant cell walls: I. The hemicelluloses of the walls of suspension-cultured sycamore cells. Plant Physiology 1973;51:174–85.
[109] Goodwin TW, Mercer EI. Introduction to plant biochemistry: the plant cell wall. New York: Pergamon Press; 1983.
[110] Severian D. Polysaccharides: structural diversity and functional versatility. 2nd ed. New York: Marcel Dekker; 2008.
[111] Charlton W, Haworth WN, Peat S. A revision of the structural formula of glucose. Journal of the American Chemical Society 1926;13:89–101.
[112] Chu SSC, Jeffrey GA. The refinement of the crystal structures of β-D-glucose and cellobiose. Acta Crystallography 1968;24:830–8.
[113] Kilzer FJ, Broido A. Pyrodynamics 1965;2:151–63.
[114] Bradbury AGW, Sakai Y, Shafizadeh F. A kinetic model for pyrolysis of cellulose. Journal of Applied Polymer Science 1979;23:3271–80.
[115] Piskorz J, Radlein D, Scott DS. On the mechanism of the rapid pyrolysis of cellulose. Journal of Analytical and Applied Pyrolysis 1986;9:121–37.
[116] Agrawal RK. Kinetics of reactions involved in pyrolysis of cellulose Part I. The three-reaction model. Canadian Journal of Chemical Engineering 1988;66:403–12.
[117] Alves SS, Figueiredo, JL JL. Pyrolysis kinetics of lignocellulosic materials by multi-stage isothermal thermogravimetry. Journal of Analytical and Applied Pyrolysis 1988;17(1988):37.
[118] Conesa JA, Cabollero JA, Marcillar A, Font R. Analysis of different kinetic mode, in the dynamic pyrolysis of cellulose. Thermochimica Acta 1995;254: 175–92.
[119] Liao YF. Mechanism study of cellulose pyrolysis. PhD thesis, Zhejiang University, Hangzhou, China, 2003.
[120] Hosoya T, Kawamoto H, Saka S. Different pyrolytic pathways of levoglucosan in vapor- and liquid/solid-phases. Journal of Analytical and Applied Pyrolysis 2008;83:64–70.
[121] Kawamoto K, Morisaki H, Saka S. Secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass. Journal of Analytical and Applied Pyrolysis 2008. http://dx.doi.org/10.1016/j.jaap.2008.08.009.
[122] Shafizadeh F, Furneaux RH, Cochran TG, Scholl JP, Sakai Y. Production of levoglucosan and glucose from pyrolysis of cellulosic materials,. Journal of Applied Polymer Science 1979;23:3525–39.
[123] Richards GN. Glycoaldehyde from pyrolysis of cellulose. Journal of Analytical and Applied Pyrolysis 1987;10:251–5.
[124] Shen DK, Gu S. The mechanism for thermal decomposition of cellulose and its main products. Bioresource Technology 2009;100:6496–504.
[125] Li S, Lyons-Hart J, Banyasz J, Shafer K. Real-time evolved gas analysis by FTIR method: an experimental study of cellulose pyrolysis. Fuel 2001;80: 1809–17.
[126] Shafizadeh F, Lai YZ. Thermal degradation of 1,6-anhydro-β-D-glucopyranose. Journal of Organic Chemistry 1972;37:278–84.
[127] Dynamotive BioOil Information Booklet, Dynamotive energy system corporation, Suite 140, 13091 Vanier Place, Richmond BC, Canada, 2011. 〈http://www.dynamotive.com/industrialfuels/biooil/〉.
[128] Banyasz JL, Li S, Lyons-Hart JL, Shafer KH. Cellulose pyrolysis: the kinetics of hydroxyacetaldehyde evolution. Journal of Analytical and Applied Pyrolysis 2001;57:223–48.
[129] Li S, Xu S, Liu S, Yang C, Lu Q. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. Fuel Processing Technology 2004;85:1201–11.
[130] Kim SJ, Jung SH, Kim JS. Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. Bioresource Technology 2010;101:9294–300.
[131] Predel M, Kaminsky W. Pyrolysis of rape-seed in a fluidized-bed reactor. Bioresource Technology 1998;66:113–7.
[132] Dai XW, Wu CZ, Li HB, Chen Y. The fast pyrolysis of biomass in CFB reactor. Energy & Fuels 2000;14:552–7.
[133] Lee KH, Kang BS, Park YK, Kim JS. Influence of reaction temperature, pretreatment, ad char removal system on the production of bio-oil from rice straw by fast pyrolysis, using a fluidized bed. Energy & Fuels 2005;19: 2179–84.
[134] Carlson TR, Vispute TP, Huber GW. Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. ChemSusChem 2010;1:397–400.

[135] Gercel HF. Production and characterization of pyrolysis liquids from sunglower-pressed bagasse. Bioresource Technology 2002;85:113–7.
[136] Sensoz S, Angin D, Yorgun S. Bio-oil production from an oilseed crop: fixed-bed pyrolysis of rapeseed. Energy Sources 2000;22:891–901.
[137] Sensoz S, Demiral I, Gercel HF. Olive bagasse (*Olea europea L.*) pyrolysis. Bioresource Technology 2006;97:429–36.
[138] Robinson JP, Snape CE, Kingman SW, Shang H. Thermal desorption and pyrolysis of oil contamined drill cutting by microwave heating. Journal of Analytical and Applied Pyrolysis 2008;81:27–32.
[139] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy & Fuels 2006;20:848–89.
[140] Williams PT, Nugranad N. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 2000;25:493–513.
[141] Abnisa F, Wan Daud WMA, Husin WNW, Sahu JN. Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in pyrolysis process. Biomass and Bioenergy 2011;35:1863–72.
[142] Di Blasi C. Modelling chemical and physical processes of wood and biomass pyrolysis. Progress in Energy and Combustion Science 2008;34:47–90.
[143] Jung S-H, Kang B-S, Kim J-S. Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. Journal of Analytical and Applied Pyrolysis 2008;82:240–7.
[144] Wang L, Cen L. Mechanism study of cellulose rapid pyrolysis. Industrial & Engineering Chemistry Research 2004;43:5605–10.
[145] Ates F, Aslı Isıkdag M. Influence of temperature and alumina catalyst on pyrolysis of corncob. Fuel 2009;88:1991–7.
[146] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils—state of the art for the end user. Energy & Fuels 1999;13:914–21.
[147] Wang Z, Guo Q, Liu X, Cao C. Low temperature pyrolysis characteristics of oil sludge under various heating conditions. Energy & Fuels 2007;21:957–62.
[148] Babich IV, van der Hulst M, Lefferts L, Moulijn JA, O'Connor P, Seshan K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. Biomass and Bioenergy 2011;35:3199–207.
[149] Garcia V, Catala-Gregori P, Hernandez F, Megias MD, Madrid J. Effect of formic acid and plant extracts on growth, nutrient digestibility, intestine mucosa morphology, and meat yield of broilers. Journal of Applied Poultry Research 2007;16:555, http://dx.doi.org/10.3382/japr.2006-00116.
[150] Gercel HF. The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake. Biomass and Bioenergy 2002;23:307–14.
[151] Pattiya A. Bio-oil production via fast pyrolysis of biomass residues from cassava plants in a fluidized-bed reactor. Bioresource Technology 2011;102: 1959–67.
[152] Chen T, Wu C, Liu R, Fei W, Liu S. Effect of hot vapor filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor. Bioresource Technology 2011;102:6178–85.
[153] Acikgoz C, Kockar OM. Characterization of slow pyrolysis oil obtained from linseed (*Linum usitatissimum L.*). Journal of Analytical and Applied Pyrolysis 2009;85:151–4.
[154] Lee HI, Park HJ, Park YK, Hur JY, Jeon JK, Kim JM. Synthesis of highly stable mesoporous aluminosilicates from commercially available zeolites and their application to the pyrolysis of woody biomass. Catalysis Today 2008;132:68–74.
[155] Park HJ, Dong JI, Jeon JK, Park YK, Yoo KS, Kim SS, et al. Effects of the operating parameters on the production of bio-oil in the fast pyrolysis of Japanese larch. Chemical Engineering Journal 2008;143:124–32.
[156] Demirbas A. Biorefineries: current activities and future developments. Energy Conversion and Management 2009;50:2782–801.
[157] Salema AA, Ani FN. Microwave induced pyrolysis of oil palm biomass. Bioresource Technology 2011;102:3388–95.
[158] Heo HS, Park HJ, Yim JH, Sohn JM, Park J, Kim SS, et al. Influence of operational variables on fast pyrolysis of Miscanthus sinensis var. Purpurascens Bioresour Technol 2010;101:3672–7.
[159] Tian Y, Zuo W, Ren Z, Chen D. Estimation of a novel method to produce bio-oil from sewage sludge by microwave pyrolysis with consideration of efficiency and safety. Bioresource Technology 2011;102:2053–61.
[160] Putun AE, Ozbay N, Apaydın-Varol E, Uzun BB, Ates F. Rapid and slow pyrolysis of pistachio shell: effect of pyrolysis conditions on the product yields and characterization of the liquid product. International Journal of Energy Research 2007;31:506–14.
[161] Fassinou W, Van de Steene L, Tourea S, Volle G, Girard P. Pyrolysis of Pinus pinaster in a two-stage gasifier: influence of processing parameters and thermal cracking of tar. Fuel Processing Technology 2009;90:75–90.
[162] Cornelissen T, Yperman J, Reggers G, Schreurs S, Carleer R. Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value. Fuel 2008;87:1031–41.
[163] Oasmaa A, Meier D. Characterisation, analysis, norms and standards. In: Bridgwater AV, editor. Fast Pyrolysis of Biomass: A Handbook, vol. 3. United Kingdom: CPL Press; 2005. p. 19–59.
[164] Ozcimen D, Karaosmanoglu F. Production and characterization of bio-oil and biochar from rapeseed cake. Renew Energy 2004;29:779–87.
[165] He R, Ye XP, English BC, Satrio JA. Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties. Bioresource Technology 2009;100:5305–11.
[166] Bridgwater AV. The production of biofuels and renewable chemicals by fast pyrolysis of biomass. International Journal of Global Energy 2007;27: 160–203.
[167] Luque R, Herrero-Davilla L, Campelo JM, Clark JH, Hidalgo JM, Luna D, et al. Biofuels: a technological perspective. Energy & Environmental Science 2008;1:542–64.
[168] Guo XY, Yan YJ, Ren ZW. The using and forecast of catalyst in bio-oil upgrading. Acta Energiae Solaris Sinica 2003;124:206–12.
[169] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management 2007;48: 87–92.
[170] Elliott DC, Neuenschwander GG. Developments in thermochemical biomass conversion. London: Blackie Academic and Professional; 1996.
[171] Zheng JL, Wei Q. Improving the quality of fast pyrolysis bio-oil by reduced pressure distillation. Biomass and Bioenergy 2011;35:1804–10.
[172] Duan P, Savage PE. Upgrading of crude algal bio-oil in supercritical water. Bioresource Technology 2011;102:1899–906.
[173] Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Lappas AA, Pilavachi PA. In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. Bioresource Technology 2011;102:8261–7.
[174] Cui HY, Wang JH, Wei SQ, Zhuo SP, Li ZH, Wang LH, et al. Upgrading bio-oil by esterification under supercritical CO2 conditions. Journal of Fuel Chemistry and Technology 2010;38:673–8.
[175] Blanchard LA, Brennecke JF. Esterfiiation of acetic acid with ethanol in carbon dioxide. Green Chemistry 2001;3:17–9.
[176] Lohitharn N, Shanks BH. Upgrading of bio-oil: effect of light aldehydes on acetic acidremoval via esterification. Catalysis Communications 2009;11: 96–9.
[177] Zhang Q. Upgrading bio-oil over solid acid and base by catalytic esterification. Hefei: University of Science and Technology of China; 2006.
[178] Xiong WM, Fu Y, Lai DM, Guo QX. Upgrading of bio-oil via esterification catalysted with acidic ion-exchange resin. Chemical Journal of Chinese Universities 2009;30:1754–8.
[179] Peng J, Chen P, Lou H, Zheng X. Upgrading of bio-oil over aluminum silicate in supercritical ethanol. Energy & Fuels 2008;22:3489–92.
[180] Peng J, Chen P, Lou H, Zheng X. Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol. Bioresource Technology 2009;100:3415–8.
[181] Tang Z, Lu Q, Zhang Y, Zhu X, Guo Q. One step bio-oil upgrading through hydrotreatment, esterification, and cracking. Industrial & Engineering Chemistry Research 2009;48:6923–9.
[182] Horne PA, Williams PT. Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields. Fuel 1996;75:1043–50.
[183] Olazar M, Aguado R, Bilbao J, Barona A. Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst. AIChE Journal 2000;46: 1025–33.
[184] Yu W, Tang Y, Mo L, Chen P, Lou H, Zheng X. One-step hydrogenation-esterification of furfural and acetic acid over bifunctional Pd catalysts for bio-oil upgrading. Bioresource Technology 2011;102:8241–6.
[185] Holbein BE, Stephen JD, Layzell DB. Canadian Pyrolysis Initiative: new directions in biorefining (working paper), BIOCAP Canadian foundation. Ontario 2005.
[186] Stephanidis SD, Nitsos C, Kalogiannis K, Iliopoulou EF, Lappas AA, Triantafyllidis KS. Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: effect of hydrothermal pre-treatment of biomass. Catalysis Today 2011;167: 37–45.
[187] Brown RC. Biorenewable resources engineering new products from agriculture. Ames IA: Iowa State Press; 2003.
[188] Li L, Zhang H. Preparing levoglucosan derived from waste material by pyrolysis. Energy Sources 2004;26:1053–9.
[189] Bennett NM, Helle SS, Duff SJB. Extraction and hydrolysis of levoglucosan from pyrolysis oil. Bioresource Technology 2009;100:6059–63.
[190] Marsman JH, Wildschut J, Mahfud F, Heeres HJ. Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection. Journal of Chromatography A 2007;1150:21–7.
[191] USEPA. Furfural. pesticide fact sheet. United States Environmental Protection Agency. Office of prevention pesticide and toxic substance (7501P), 2006.